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"Template-Preparation and Characterization of Semiconductor Nanorod Organosols"

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**TEMPLATE-PREPARATION AND CHARACTERIZATION OF SEMICONDUCTOR
NANOROD ORGANOSOLS**

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ABSTRACT

The template method was used to prepare organosols composed of either CdS nanorods (diameter = 45 nm or 90 nm) or ZnO nanorods (diameter = 90 nm). Polycarbonate track-etched filters were used as the template membranes. After template synthesis, the nanorods were released from the template membrane and dispersed in chloroform. The stability of these nanorod organosols was monitored using UV-visible absorption spectroscopy. The 90 nm-diameter CdS nanorod organosols were found to be more stable than the 90 nm-diameter ZnO nanorod organosols. In addition, the 45 nm-diameter CdS organosols were found to be more stable than the larger 90 nm-diameter CdS sols. The nanorods that comprise these sols were characterized by electron microscopy, energy dispersive spectroscopy, electron diffraction and powder X-ray diffraction.

INTRODUCTION

Recently, we reported on the preparation of gold and silver nanorod sols in nonaqueous solvents (organosols).¹ The Ag and Au nanorods were prepared via the template method,² and sols were obtained by simply dissolving the polymeric template membrane in an organic solvent and dispersing the liberated nanorods in this solvent. A similar approach was used to prepare water-based Au nanorod sols.³ We are interested in sols of template-synthesized nanostructures because we would like to use these nanostructures as building blocks to self-assemble supramolecular architectures.⁴ In this correspondence, we extend this sol-preparation method to template-synthesized nanorods composed of semiconductors.

The template method entails the synthesis of a desired material within the pores of a microporous membrane.² The membranes employed have cylindrical pores with monodisperse diameters, and corresponding cylindrical nanostructures are obtained. Electrochemical deposition of materials into the pores of such membranes has proven to be a particularly powerful approach for preparing such cylindrical structures.^{1,2,4} The key advantage of electrochemical template synthesis is that the aspect ratio (length/diameter) of the resulting cylindrical nanostructures can be controlled at will. The aspect ratio can be varied by changing the amount of charge used to deposit the cylindrical nanostructures within the pores, thereby changing the length of the nanostructures obtained. Alternatively, the pore diameter in the template membrane can be changed, thereby changing the diameter of the resulting nanostructures.

Because of this ability to control the aspect ratio of the cylindrical nanostructures obtained, the electrochemical template approach allows for the preparation of colloids consisting of cylindrical particles with any desired aspect ratio. We have been especially interested in

"nanorods" (cylinders with aspect ratios in the range from 1 to ~30 nm), because our prior work showed that these relatively low aspect-ratio materials form the most stable colloidal suspensions.¹ We have used electrochemical synthetic methods to deposit nanorods composed of two semiconductors, CdS and ZnO, within the pores of microporous polycarbonate template membranes. Semiconductor nanorods with two different diameters were prepared. These nanorods were then suspended in CHCl_3 and the stability of the resulting organosols was monitored using UV-visible absorption spectroscopy.¹

EXPERIMENTAL

Template Synthesis of CdS and ZnO Nanorods. Polycarbonate "track-etch" membranes with nominal pore diameters of 15 nm and 30 nm were obtained from Corning. CdS nanorods were deposited into the pores of these template membranes using a previously reported pulsed electrolysis procedure.⁵ An aqueous solution of 0.2 M CdCl_2 (anhydrous, Fisher Scientific) and 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$ (anhydrous, Fisher Scientific) which was adjusted to pH=2 with HCl (Mallinckrodt) was used to electrodeposit the CdS. The deposition took place at elevated temperatures (65°C to 75°C) under a N_2 (Air Liquide) atmosphere by applying a cathodic pulse = -0.95 V vs. Ag/AgCl for 1 s followed by the application of an anodic pulse = 0.6 V vs. Ag/AgCl for 2 s. These pulses were applied in a continuous cycle for 30 minutes.⁵

ZnO nanorods were deposited into the pores of the polycarbonate template membranes by an aqueous deposition method previously reported by Lincot and Peulon.^{6,7} Briefly, ZnO was cathodically deposited at -0.85 V vs. Ag/AgCl from a 5 mM ZnCl_2 (Mallinckrodt) and 0.1 M KCl electrolyte (Mallinckrodt) solution saturated with O_2 (Air Liquide). The ZnO nanorods were

electrodeposited at 75 to 80°C for 30 minutes. All aqueous solutions were prepared with Milli-Q 18 M Ω H₂O.

The electrochemical depositions were performed using an EG&G PAR Model 173 potentiostat in combination with an EG&G PAR Model 179 digital coulometer or an EG&G PAR Model 273 potentiostat. Both ZnO and CdS depositions took place in a water bath adjusted to the appropriate temperature. In order to electrochemically deposit the semiconductors into the pores of these polycarbonate membranes, a cathode must be applied to one face or surface of the membrane. This was accomplished by evaporating Au (99.99 %, Aldrich) using a Denton Vacuum DV502A evaporator; this Au-film cathode was approximately 0.5 μ m thick.

The Au-coated template membrane was then clamped between a glass plate and a section of glass tubing (25-mm diameter) which terminated with an O-ring joint. The Au surface was placed face down on the glass plate. The tubing served as the electrochemical cell and the O-ring (32-mm diameter) determined the area of the template membrane into which the semiconductor was deposited. A piece of conductive Cu tape was attached to the Au membrane surface to provide a working electrode contact. In addition, a Ag/AgCl reference electrode (BAS RE-5) and a Pt/Rh gauze counter electrode (Alfa Aesar) were placed in the cell for each electrochemical deposition.

Characterization of CdS and ZnO Nanorods. The semiconductor nanorods were analyzed using scanning (SEM) and transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), electron diffraction, and powder X-ray diffraction (XRD). SEMs were obtained on a Phillips 505 microscope. The semiconductor nanorods were isolated by dissolving the template membrane in CHCl₃ and filtering the resulting sol through an alumina filter (0.2 μ m pore diameter, Whatman). This left the nanorods isolated on the surface of the filter. The

collected nanorods were washed with CHCl_3 to remove residual polycarbonate and sputtered with 5 nm of Au prior to SEM to prevent charging of the sample.

TEMs and electron diffraction were taken on a JEOL JEM-2000 EX-II electron microscope. The camera length for the electron diffraction was 80 cm. TEM samples were prepared by depositing the nanorod sol dropwise onto a C-coated Cu TEM grid and imaged without further preparation. EDS data were collected using a Kevex Super 8000 microanalysis system equipped with a Li drifted Si detector that was attached to the SEM. SEM samples used for the EDS analysis were not sputtered with Au. Powder XRD patterns were obtained using an Enraf Nordas FR552 camera with a $\text{Cu K}\alpha$ anode.

Preparation of the CdS and ZnO Nanorod Organosols. After the electrodeposition of CdS or ZnO into the pores of the polycarbonate membrane, the Au cathode was removed from the membrane by wiping with a laboratory tissue wetted with methanol (ACS grade; Fisher Scientific). The semiconductor/template membrane composite was washed with H_2O and dried in an oven at 70°C . This composite membrane was then immersed in CHCl_3 (Fisher Scientific, ACS grade) and manually shaken for 10 seconds to dissolve the membrane. The organosol was simply the resulting dispersion of the freed nanorods in this solvent. Typically, one circular piece of membrane (25-mm diameter) containing the deposited nanorods was dissolved in 5 mL of CHCl_3 to form the nanorod organosol. This resulted in an organosol containing approximately 0.5 mg of semiconductor nanorods and 10 mg of polycarbonate dispersed in CHCl_3 .

Characterization of the Semiconductor Nanorod Organosols. Semiconductor colloid particles absorb UV-visible light having energy greater than their band gap.^{8,9} The band gap energy of both bulk CdS ($E_g = 2.4 \text{ eV}$) and ZnO ($E_g = 3.2 \text{ eV}$) is quite large; therefore, both of these

semiconductor colloids can be characterized by UV-visible absorption spectroscopy.¹⁰ These semiconductor colloids have absorption spectra which not only helps to characterize the material, but also provides a convenient route for monitoring the stability of the nanorod sols fabricated. The stability of the sols was assessed by monitoring this absorbance as a function of time. For CdS sols, the shoulder observed near 450 nm was monitored versus time, while for ZnO organosols the λ_{max} at 335 nm was used. These UV-visible spectra were taken on a Hewlett Packard 8452A diode array spectrophotometer.

RESULTS AND DISCUSSION

Preparation and Characterization of the CdS Nanorods. We and others have used electrosynthetic methods to deposit semiconductor nanostructures within the pores of microporous template membranes; however, in all cases alumina template membranes were employed.¹¹⁻¹³ Chemical synthetic methods have also been used to deposit semiconductors within the pores of such alumina template membrane.^{14,15} These chemical synthetic methods typically yield cylindrical nanostructures that extend the complete thickness (tens of microns) of the template membrane; i.e., the aspect ratio cannot be varied using such synthetic methods. As per our prior work,¹ commercially-available polymeric templates were used to prepare the semiconductor nanorods. Organosols were prepared by simply dissolving the nanorod-containing template membrane into CHCl_3 to free and disperse the nanorods.¹

The half reaction responsible for CdS deposition within the pores of these membranes is shown in Equation 1.¹⁶

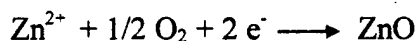


Figure 1A shows a scanning electron micrograph (SEM) of typical 90 nm-diameter CdS nanorods. Such SEMs indicate that these nanorods are $2.2 \mu\text{m} \pm 0.4 \mu\text{m}$ in length with an aspect ratio of 24. The nanorods were analyzed by energy dispersive spectroscopy (EDS) to confirm that the material deposited was, indeed, CdS. The EDS spectrum shows the presence of both Cd (emissions at 3.1 keV and 3.3 keV) and S (emission at 2.3 keV) (Figure 1B).

These CdS nanorods were also characterized by electron diffraction (Figure 1C). The inner ring of the acquired electron diffraction pattern is indexed to the three reflections of (100), (002), and (101) for hexagonal CdS.¹⁷ The middle ring is identified as the (110) reflection. The outer ring is due to the (112) reflection for CdS. This electron diffraction pattern is identical to the pattern previously observed for CdS suspensions synthesized in micellar media and indicates that these nanorods consist of polycrystalline CdS.¹⁷ Polycrystalline material was also obtained when this pulsed-electrolysis method was used to deposit CdS thin films.⁵

In addition to preparing 90 nm-diameter nanorods, smaller 45 nm-diameter CdS nanorods have also been prepared (Figure 2). These smaller nanorods were also determined to be hexagonal CdS and had an aspect ratio of approximately 22.

Preparation and Characterization of the ZnO Nanorods. ZnO was cathodically deposited at a constant potential of -0.85 V vs. Ag/AgCl. This deposition is similar to that reported by Peulon and Lincot who obtained ZnO films from aqueous O₂-containing ZnCl₂ solutions (Equation 2).^{6,7}



(2)

The resulting 90 nm-diameter ZnO nanorods had an average length of $2.5 \mu\text{m} \pm 0.3 \mu\text{m}$ with an aspect ratio of 28 (Figure 3A). The EDS of these nanorods (Figure 3B), confirmed the presence

of Zn (emissions at 1.0 keV, 8.6 keV, and 9.6 keV). However, EDS spectra always show the presence of O; therefore, the composition of these nanorods could not be confirmed by EDS. The composition was verified via powder XRD (Figure 3C). This pattern displays three peaks at 32° , 34° , and 36° 2θ that were assigned to the (100), (002), and (101) reflections for hexagonal ZnO.^{6,7} The crystal structure of these ZnO nanorods is identical to the crystalline structure of the electrodeposited ZnO films prepared by Lincot and Peulon.^{6,7}

CdS and ZnO Nanorod Organosols. The organosols obtained from these nanorods show UV-visible absorption spectra corresponding to bulk ZnO and bulk CdS (Figure 4).^{8,9,18,19} For example, the onset of absorbance near 600 nm for the 90-nm diameter CdS nanorods (Figure 4, spectrum [A]) corresponds to bulk CdS with a band gap energy of 2.5 eV.^{18,20} In addition, the λ_{max} at 335 nm (Figure 4, spectrum [C]) is characteristic of bulk ZnO with a band gap energy of 3.2 eV.^{19,21,22} These nanorod sols do not show quantum confinement properties in the absorption spectra because of their relatively large size.¹⁸ The CdS nanorod sols had the characteristic yellow color that is well known for CdS colloids.^{8,9,18} The ZnO organosols were opalescent in appearance.

The number of nanorods in the 45-nm and 90-nm CdS sols are approximately the same because the pore density in the two template membranes used to prepare these sols is the same, and the same area of membrane was dissolved to obtain each sol. Furthermore, the aspect ratios of the 45-nm and 90-nm diameter CdS nanorods are approximately the same. However, because of the smaller diameter, a smaller total amount of CdS is dispersed in the 45-nm sol. As result, the absorbance of the 90-nm sol (Figure 4, spectrum [A]) is greater than that of the 45-nm sol (Figure 4, spectrum [B]).

The stability of both the CdS and ZnO nanorod organosols was studied by monitoring the change in absorption intensity as a function of time.¹ Curve [1] in Figure 5 shows the stability of the 90-nm CdS sols. Approximately 50% of the nanorods precipitate after four days. However, after this initial precipitation, these sols are stable for periods as long as two weeks (Inset Figure 5). The 45-nm CdS sols are much more stable (curve [2] in Figure 5). Only about 20% of the initially dispersed nanorods are lost to precipitation after 4 days.

The 90-nm ZnO sols are the least stable (Figure 5A, Curve [3]). After four days, ca. 75% of these nanorods had precipitated from the sol, and after five days essentially all of the ZnO had precipitated. Dispersing the ZnO nanorods in a different organic solvent, hexafluoroisopropanol, did not help increase the stability of the ZnO organosol. Furthermore, the addition of the polymeric stabilizer, polyvinylacetate, did not enhance the stability. The particles in these 90-nm ZnO sols have a slightly larger aspect ratio than the particles in the corresponding 90-nm CdS sols (24 for CdS; 28 for ZnO), and our prior work has shown that stability decreases with increasing aspect ratio.¹ However, the molecular mass of CdS is significantly larger than that of ZnO, so from this standpoint, the CdS sols might be expected to be less stable. The reason for the lower stability for the ZnO sols is currently not understood.

CONCLUSIONS

Template synthesis can be used to prepare semiconductor nanorod organosols of CdS and ZnO in CHCl_3 . The CdS nanorod organosols were shown to be more stable than ZnO organosols. In addition, the smaller 45-nm-diameter CdS nanorods sols were more stable than the larger 90-nm-diameter CdS sols. The CdS nanorods sols remain stable for up to two weeks.

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FIGURE CAPTIONS

Figure 1 Characterization of the 90 nm diameter CdS nanorods isolated from the corresponding nanorod organosol. (A) Scanning electron micrograph. (B) Energy dispersive spectrum. (C) Electron diffraction pattern. The camera length was 80 cm and an accelerating voltage of 100 kV was used.

Figure 2 Transmission electron micrograph of 45 nm diameter CdS nanorods isolated from the nanorod organosol.

Figure 3 Analysis of the 90 nm diameter ZnO nanorods isolated from the corresponding nanorod organosol. (A) Scanning electron micrograph. (B) Energy dispersive spectrum. (C) Powder X-ray diffraction pattern.

Figure 4 UV-visible spectra of the semiconductor nanorod organosols prepared in CHCl_3 . [A] 90 nm-diameter CdS nanorod sol. [B] 45 nm-diameter CdS nanorod sol. [C] 90 nm-diameter ZnO nanorod sol. The spectra were taken four hours after the sols were prepared.

Figure 5 Plot of absorbance versus time (stability plot) for the various semiconductor nanorod organosols. [1] 90 nm-diameter CdS nanorod sol. [2] 45 nm-diameter CdS nanorod sol. [3] 90-nm diameter ZnO nanorod sol. Inset, longer time stability plot for the 90 nm-diameter CdS nanorod sol.

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Figure 1A

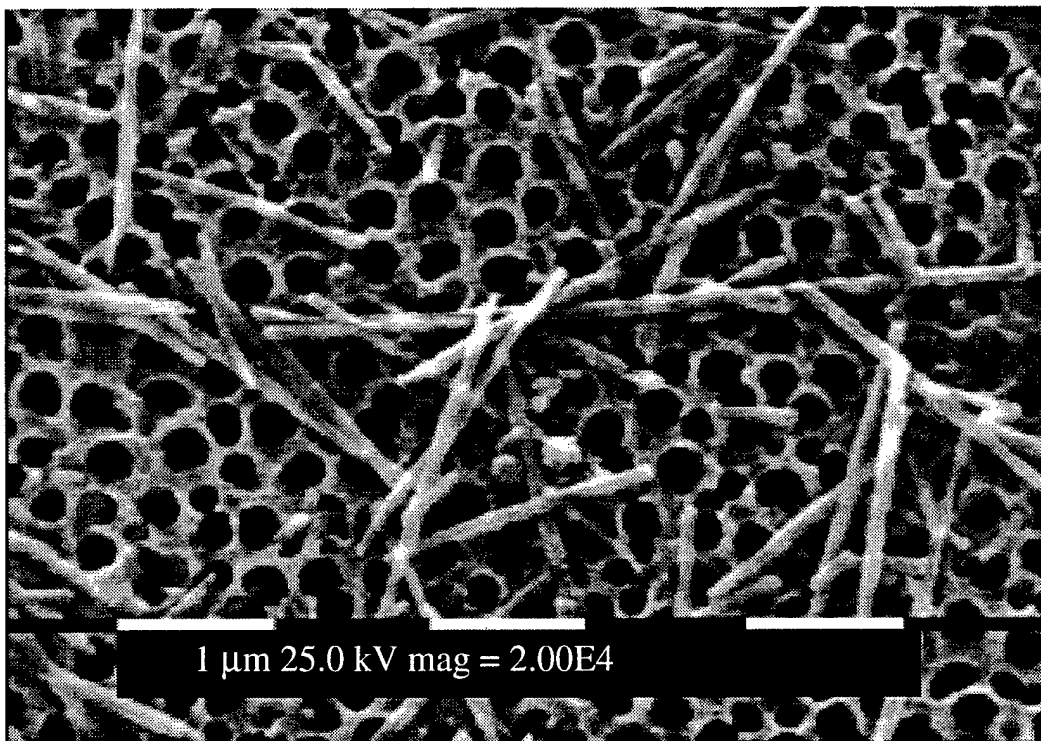


Figure 1B

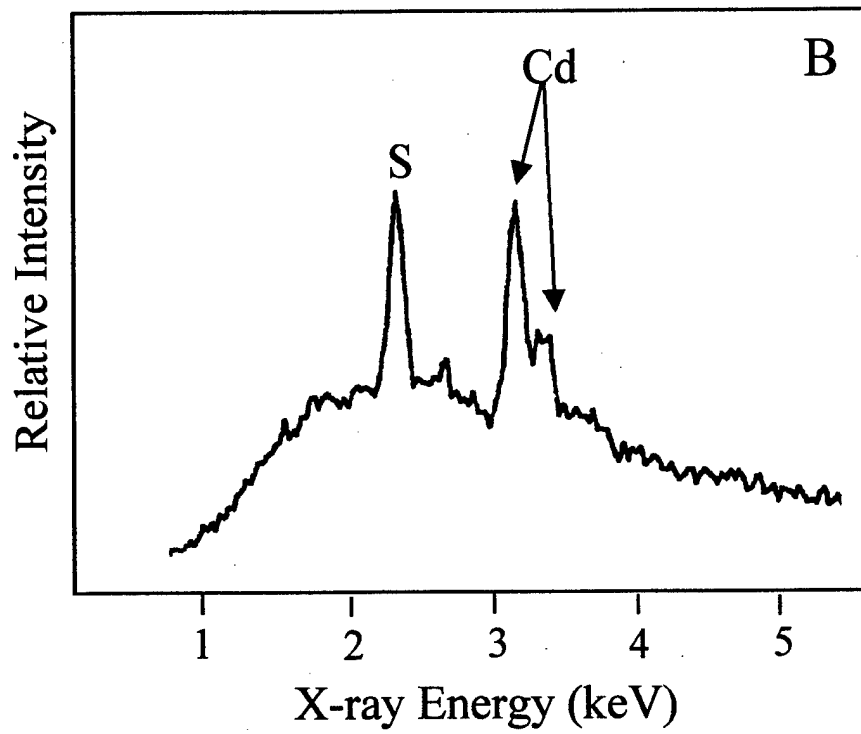


Figure 1C

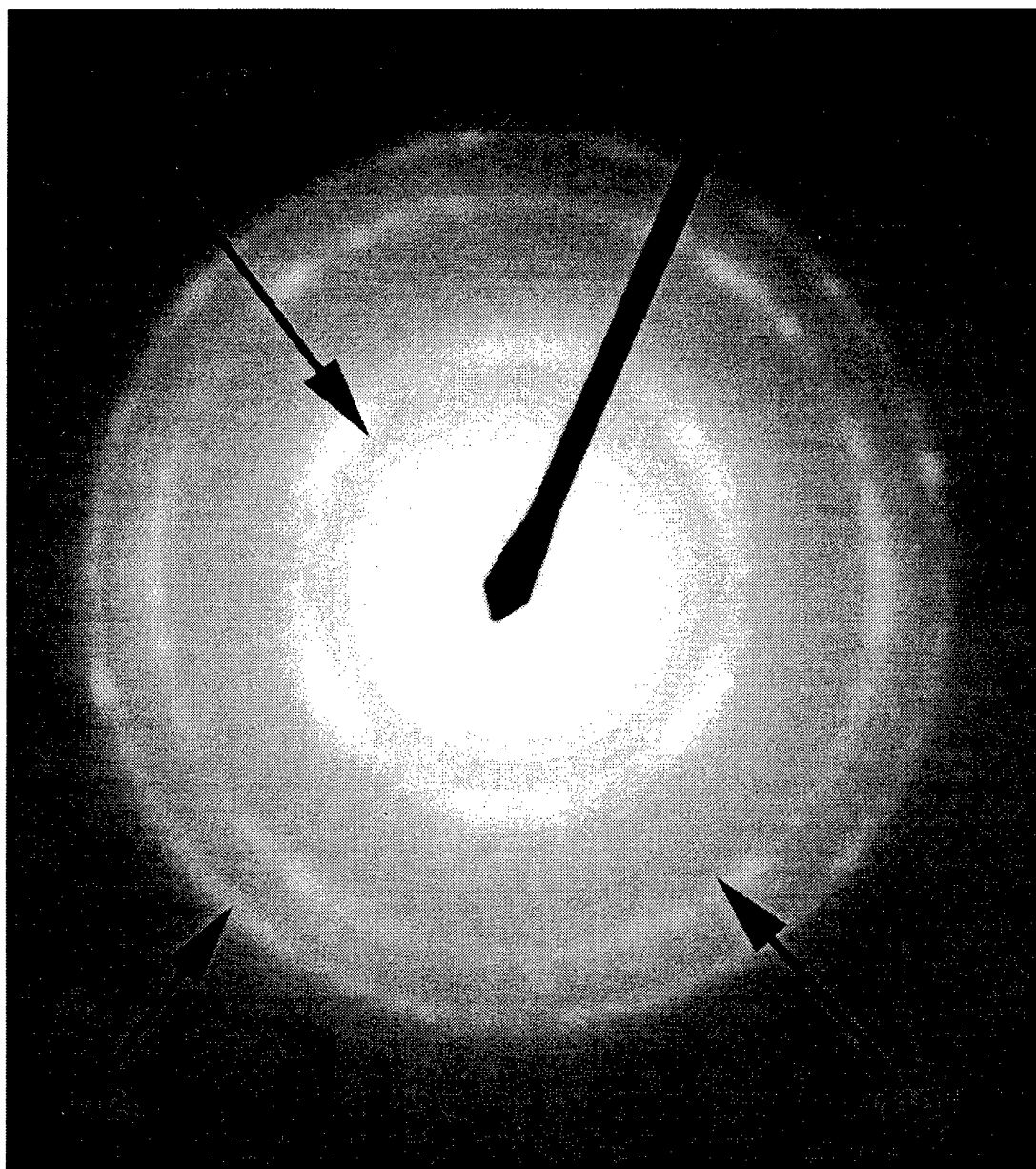


Figure 2

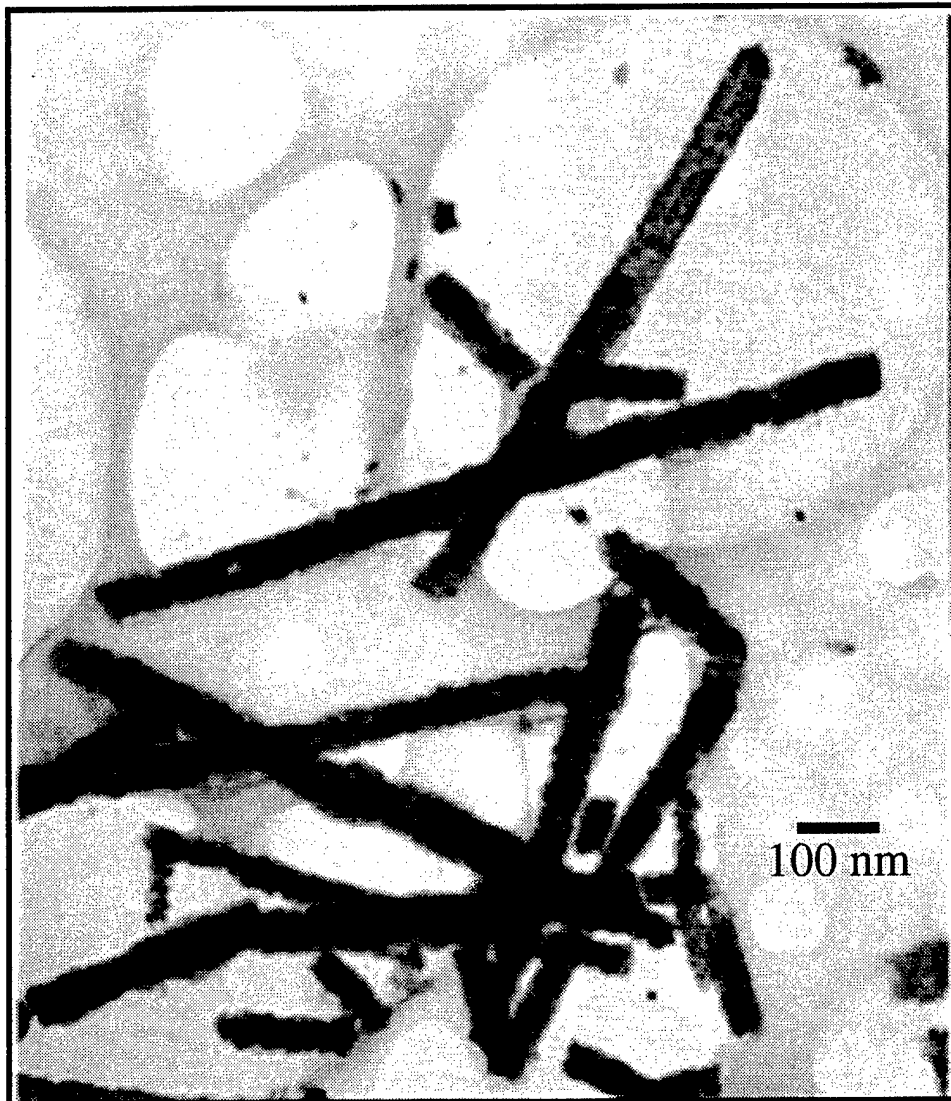
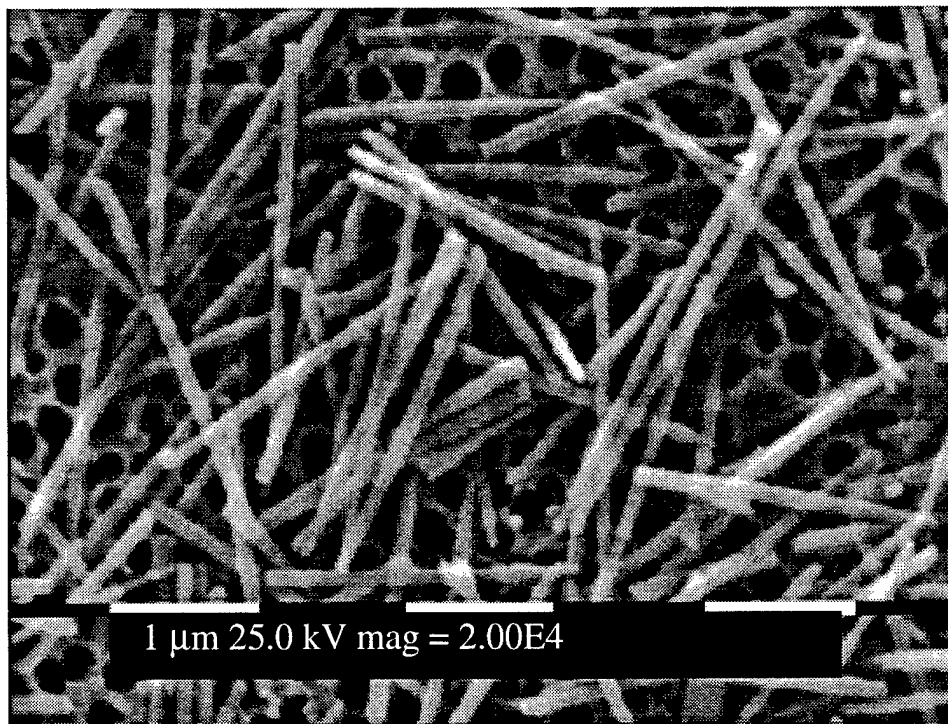


Figure 3A



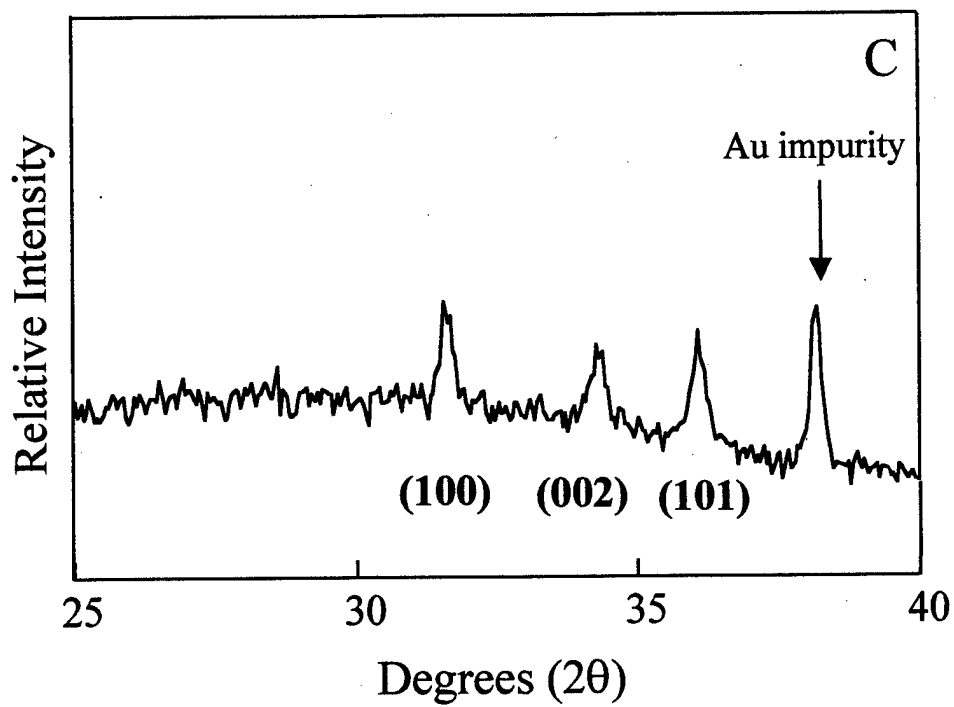
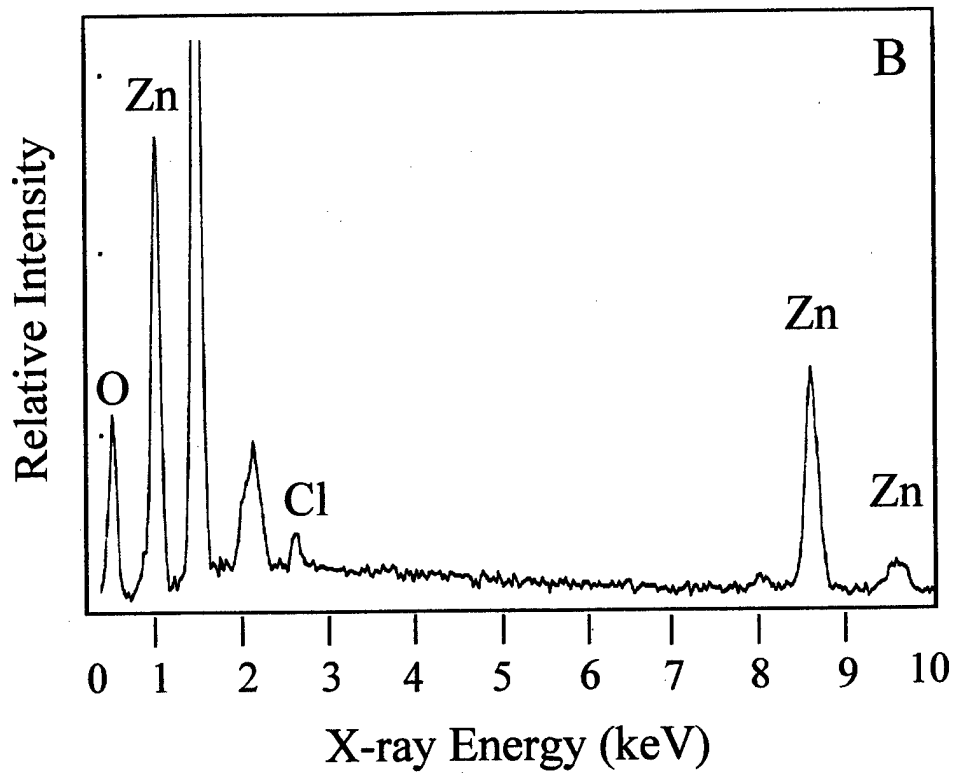


Figure 4

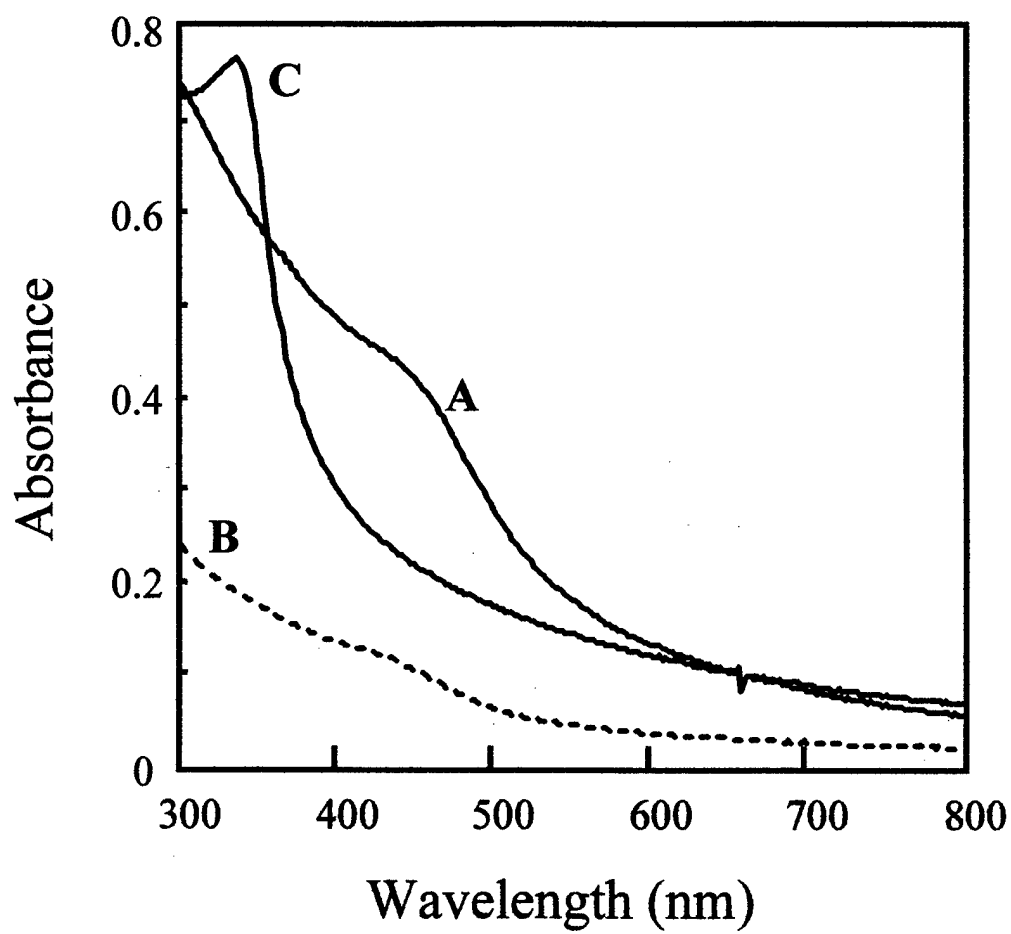


Figure 5

